PHYSICAL REVIEW B VOLUME 31, NUMBER 10 15 MAY 1985

Thermal conductivity and thermopower of graphite at very low temperatures

D. T. Morelli and C. Uher
Physics Department, The University of Michigan, Ann Arbor, Michigan 48109

(Received 17 September 1984; revised manuscript received 25 January 1985)

Measurements of the in-plane thermal conductivity and thermopower of graphite have been performed from 70 mK to 8 K. The thermal conductivity exhibits a crossover from a T^n ($n > 2$) dependence above 1 K to a $T^{1.14\pm0.02}$ law at lower temperatures, behavior attributed to a combination of increasing carrier conduction and a lattice component varying slower than T^2 from 1 K down to about 0.3 K. The thermoelectric power is negative throughout the range; below 2 K, it is a linear function of temperature, the magnitude of the slope being proportional to the degree of structural imperfection of the samples.

I. INTRODUCTION

Interest in the properties of graphite, in its many forms, has grown considerably in recent years, mainly due to its technological promise as a very strong yet lightweight material, as well as its use as the parent material of a class of important synthetic substances known as graphite intercalation compounds. As a result, theoretical and experimental investigations are once again focused on this layered semimetal.

We report here on measurements of the in-plane thermal conductivity and thermopower of highly oriented pyrolytic graphite (HOPG) at sub-Kelvin temperatures. The results shed new light on the interplay of lattice vibrations and carriers in this hitherto uninvestigated regime. In particular, experimental evidence points to the fact that below 1 K the lattice thermal conductivity may be decaying slower than the expected T^3 power-law dependence.

II. EXPERIMENTAL

Samples used in this investigation are the same as those on which we have recently reported electrical resistivity measurements.[1] The experiments were performed in a dilution refrigerator down to about 70 mK. Thermal conductivity was measured by a steady-state technique whereby a known heat current is passed through the sample producing a temperature difference along its length. The precision of the technique is limited primarily by the resolution of the temperature difference $\Delta T = T_H - T_C$, where T_H and T_C are temperatures of the hot and cold junctions along the length of the sample. We have used calibrated germanium resistance sensors[2] (30 Ω nominal at 4.2 K) which are accurate to better than 0.5 mK resulting in an error of at most 2—3 % at the lowest temperatures. In addition, we have available a set of superconducting fixed-point standards, National Bureau of Standards—Standard Reference Material 768, serial number 68, which provide convenient reference temperature points against which the germanium thermometers are cross-checked during each cooldown. The absolute accuracy of the thermal conductivity data is limited by the uncertainty in the dimensions of the samples. This error we estimate as about 5% and the figure includes corrections for the thermal contraction in the *c*-axis direction on cooling. Thermoelectric voltage was measured with the aid of a superconducting quantum-interference device (SQUID) operating as a null detector. In this procedure, described in detail elsewhere,[3] the thermoelectric signal (V_s) across the sample is balanced by a resistive voltage produced by passing a known current (I_r) through a reference resistor (R_r) held at 4.2 K. The null condition $V_s = I_r R_r$ is measured by the SQUID to a precision of about 1 part in 10^4. The thermopower is then obtained from $S = V_s/\Delta T$, and the overall precision is again limited by the uncertainty in ΔT.

Samples used in the investigations were cut from slabs of highly oriented pyrolytic graphite (HOPG) manufactured by Union Carbide Corporation; this material represents some of the best synthetic graphite available. While it is not a single crystal, having a typical *c*-axis mosaic spread of about 1°, its *in-plane* transport properties are very similar to those of the best natural single crystals. In addition, unlike the natural single crystals, which are usually in the form of thin flakes of sizes 1—2 mm, the HOPG material is available in bulk sizes of several centimeters, making accurate thermal transport measurements more feasible and reliable. Several relevant parameters concerning the samples are given in Table I.

TABLE I. Relevant parameters of samples. RRR represents the residual resistivity ratio.

Sample no.	Dimensions (mm^3)	RRR	ρ_0 ($\Omega\,\text{cm}$)	dS/dT below 2 K ($\mu\text{V}\,\text{K}^{-2}$)
1	$2.3\times3.3\times15.5$	11.1	0.4068×10^{-5}	-1.60
2	$2.7\times5.1\times11.4$	6.5	0.8376×10^{-5}	-2.34
3	$1.2\times3.3\times9.0$	16.5	0.2866×10^{-5}	-1.17

III. RESULTS

A. Thermal conductivity

In Fig. 1 we show a log-log plot of the thermal conductivity K for two samples designated HOPG Nos. 1 and 2. For the reader's convenience we also show in the inset the behavior of the in-plane thermal conductivity extending up to room temperature. From 10 K down to 1 K, the thermal conductivity falls with a temperature dependence faster than T^2 for both samples. Such behavior has been observed previously[4–7] and can be accounted for by assuming the conduction proceeds primarily via lattice waves which interact with crystallite boundaries.[8] The temperature dependence is slightly faster than the variation of the specific heat which has been observed to transform from T^2 to T^3 in this regime.[9–11] At 1 K there is a distinct elbow in the $K(T)$ curves and below this temperature $K(T) \sim T^{1.14 \pm 0.02}$. While this undoubtedly indicates the onset of a crossover into the regime where carrier conduction dominates, the actual magnitude of the exponent is puzzling.[12] Based on our measurements of the electrical resistivity on these specimens,[1] which show that ρ varies by less than 0.5% between 0 and 1 K, it is clear that below 1 K carrier conduction is limited by impurity scattering. Consequently, the Wiedemann-Franz law (WFL), $K\rho/T = L_0 = \text{const}$, should apply, and one would expect the carrier thermal conductivity to approach a strictly linear function of temperature.

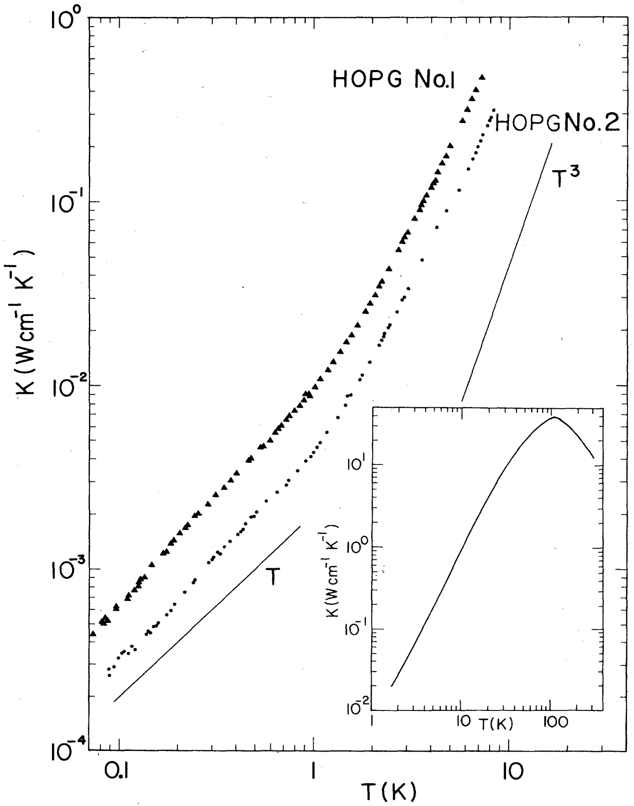

FIG. 1. Temperature dependence of the in-plane thermal conductivity of two HOPG samples. The inset shows typical behavior at higher temperatures.

The discrepancy between the expected and observed exponents of the power-law dependence is, in our opinion, associated with the phonon spectrum and has nothing to do with the charge carriers. The reasoning behind this argument is as follows. It has been shown previously,[7] and we have confirmed it independently for the present samples, that the WFL in graphite is obeyed at 4.2 K. Thus, already at these temperatures the carrier scattering assumes a substantially elastic character which, as T decreases, should be even more pronounced. Using our resistivity data in conjunction with the WFL, the carrier thermal conductivity below 4.2 K should then be given as

$$\begin{aligned} \text{HOPG No. 1: } K_{\text{carr}} &= (L_0/\rho)T \\ &= 0.0060T \ (\text{W cm}^{-1}\text{K}^{-1}) , \\ \text{HOPG No. 2: } K_{\text{carr}} &= 0.0029T . \end{aligned} \tag{1}$$

Furthermore, as shown in Fig. 3, the thermopower data below 2 K obey a perfect linear dependence with temperature (purely diffusion thermopower), supporting our position that there is nothing unexpected about the carrier spectrum or its scattering mechanism.

Assuming that Eq. (1) indeed describes correctly the temperature variation of the carrier thermal conductivity below liquid-helium temperature, the difference between the actual experimental values of $K(T)$ and K_{carr} from Eq. (1) is plotted in Fig. 2. We see that in order to account for the observed total thermal conductivity variation below 1 K, the lattice conductivity K_L would have to contain a contribution which varies slower than T^2 over a substantial fraction of this temperature regime. At the lowest temperatures, i.e., $T < 0.3$ K, there is a tendency of the lattice conduction to return to a higher power-law variation; however, note that K_L is found by taking the difference between two relatively large numbers and as such is susceptible to a large degree of error as $T \rightarrow 0$.

At this stage we can only speculate on the nature of the physical mechanism which might plausibly produce the observed temperature dependence of the lattice conduction. Since electrical resistivity as well as the purely diffusion character of the thermopower below 2 K seem to rule out a significant carrier-phonon interaction at these temperatures, it is likely that the behavior of K_L has its origin in phonon-defect and phonon-boundary scattering.[13] To explain the results shown in Fig. 2, i.e., the lattice thermal conductivity falling first quickly, then more slowly, and finally quickly again below 0.3 K, we envision two possibilities.

(i) We suppose that there is more than one type of phonon mode contributing to the heat conduction, and the particular way in which these different modes add together to produce the total conduction depends on temperature. What we have in mind, in fact, is a combination of "in-plane" phonons (both longitudinal and transverse) with "out-of-plane" phonon modes. This is the approach taken by Komatsu[10] and Kelly[8] in their descriptions of the specific heat and thermal conductivity, respectively, of graphite above 2 K. The specific heat variation of both

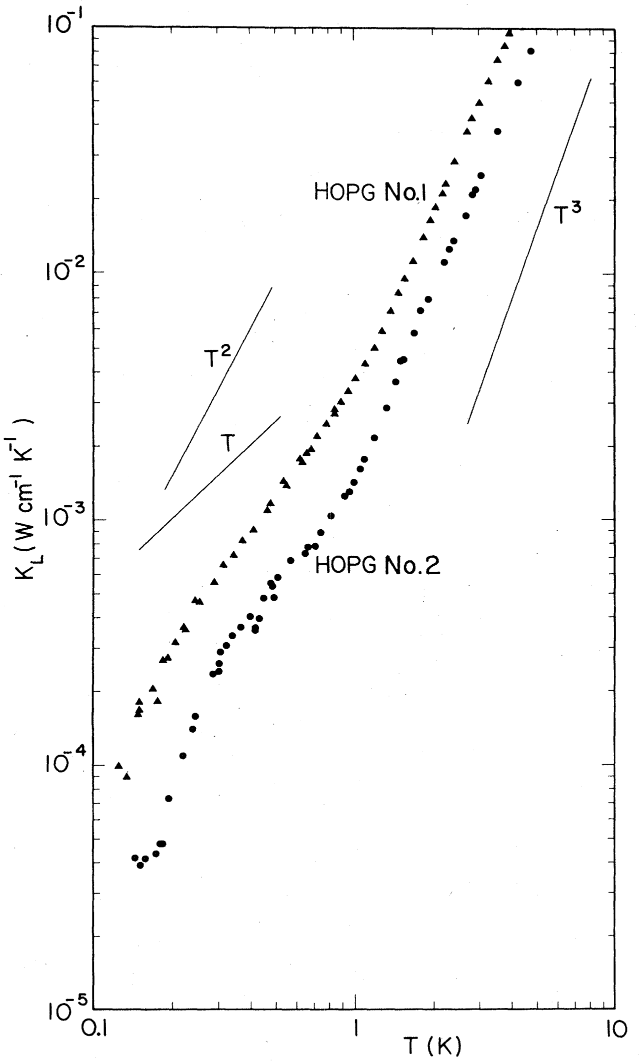

FIG. 2. Lattice component of the thermal conductivity of graphite below 4 K.

these sets of modes are known to transform from T^2 to T^3; in the case of the in-plane vibrations the specific heat contribution becomes proportional to T^3 below 25 K, whereas in the case of the out-of-plane modes the crossover is expected to occur somewhere below 2 K.[14] On the basis of this model, the lattice thermal conductivity shown in Fig. 2 can be explained as follows: We assume that scattering occurs off of microcrystallite boundaries, and we estimate that this process yields a phonon mean-free path l_0 of about 16μ for HOPG No. 1 and 5μ for HOPG No. 2 at 2 K. The thermal conductivity is then given as

$$K_L=\tfrac{1}{3}l_0\sum_i \overline{V}_i C_i \ , \tag{2}$$

where C_i is the lattice specific heat, and $\overline{V}_i$ represents the average phonon velocity of the ith phonon mode, where i runs over both in-plane and out-of-plane phonons described above. The particular way in which the velocities and specific heats of these phonon modes average together is a function of temperature. As the temperature is lowered below 4 K the thermal conductivity falls nearly as T^3 as the in-plane vibrations dominate the thermal processes in this regime. As 1 K is approached, the out-of-plane phonon modes begin to carry most of the heat and this, coupled with the fact that $\overline{V}$ for these modes is smaller, reduces the temperature dependence of the lattice conduction. Finally, near 0.3 K, the specific heat associated with these vibrations approaches a T^3 dependence, and thermal conductivity begins to decrease more rapidly. If this analysis is correct, our results on the lattice thermal conductivity lend strong support to the validity of Komatsu's two-phonon model.

(ii) A second possible explanation for the observed temperature dependence of K_L centers on details of the phonon-defect interaction. An evolution from a T^3 to a T^2 temperature dependence can arise when large-scale (extended) defects are present in the crystals, as was found in the case of NaCl containing artificially implanted silver colloids.[15,16] When the dominant phonon wavelengths are smaller than the dimensions of the defects, the latter will scatter these phonons independent of frequency and the thermal conductivity will proceed roughly as the specific heat; however, when the temperature is lowered below the value at which the dominant phonon wavelengths exceed the defect dimensions, significant Rayleigh scattering will occur and the temperature dependence of K_L will be slowed. This may be happening in graphite near 1 K. At this temperature, assuming an in-plane Debye temperature of about 2500 K,[17] and a nearest-neighbor distance of 1.42 Å,[18] the dominant phonon wavelength is about 3500 Å. Stacking faults[19] which in graphite occur as "strips" having a width of $\sim 10^3$ Å are likely candidates for such defect centers. Finally, when the temperature is lowered even further, to about 0.3 K in graphite, the phonon wavelengths approach the dimensions of the crystallite boundaries and the thermal conduction once again mimics the specific heat. In graphite any interactions of in-plane phonons with defects can play an extremely important role because of the intense "focusing" of the phonon-energy flow in the planes[20,21] due to the elastic anisotropy of its structural arrangement.[22]

While either of the above models can qualitatively account for the observed behavior, we do not rule out the possibility of other mechanisms occurring in this important material; for example, a specular, rather than diffuse nature of scattering of phonons at boundaries[23] can significantly affect the temperature dependence of the conduction. Ultimately, of course, one would like to separate the electron and lattice conductivities below 1 K by applying a transverse magnetic field. While only a very modest field strength of a few kG is needed, such measurements are complicated by the field dependence of the thermometers. It is currently an outstanding problem in low-temperature thermometry to develop a simple thermometer with the properties similar to that of carbon-glass sensors (small and reproducible magnetoresistance) but extending their useful range to well below 1 K.

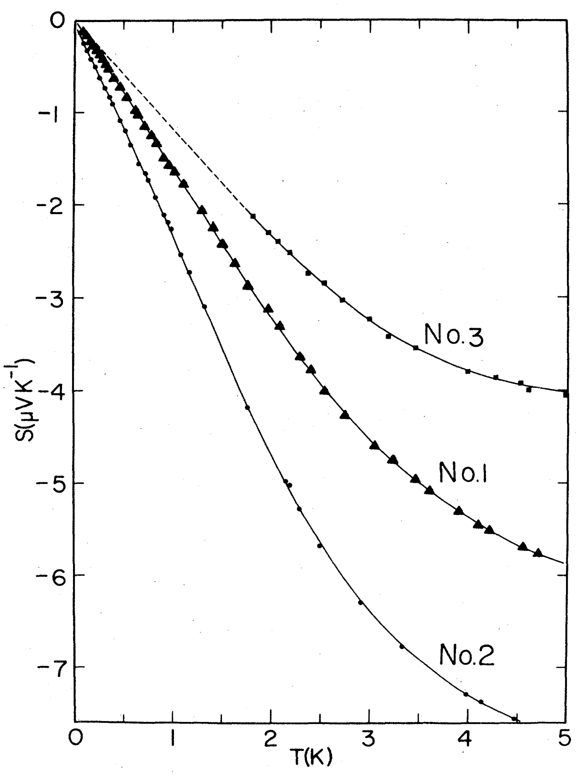

FIG. 3. Temperature dependence of the in-plane thermopower of three HOPG samples.

B. Thermoelectric power

In Fig. 3 are shown the results of measurements of the thermoelectric power of samples 1 and 2, as well as a third sample of very high quality. $S(T)$ for all samples is negative and below 2 K obeys a linear dependence. In graphite, both sets of carriers (i.e., electrons and holes) are degenerate in this temperature range, so that the thermopower is the sum of the partial thermopowers of each carrier pocket, weighted by the appropriate carrier mobilities. Since the mobilities are weakly temperature dependent in this regime, the temperature dependence of the total thermopower reflects that of the partial thermopowers of a degenerate conductor, i.e., linear in T. There is no evidence of any anomalous behavior in $S(T)$ down to the lowest temperatures. Note that the magnitude of the thermopower as well as the slope increase with decreasing sample quality. This can be accounted for by either an increase in electron concentration or an increase in the ratio of electron to hole mobility (due to changes in the scattering times) as structural imperfection increases;[24] a more definite analysis, however, would require a complete set of galvanomagnetic data. Above 2 K the curves begin to deviate from straight lines, flattening into the broad shoulder region observed by Ayache *et al.*,[25] and this is thought to be due to the onset of phonon dragging of the H-point minority holes.

IV. CONCLUSION

We have measured the in-plane thermal conductivity and thermoelectric power of HOPG at very low temperatures. The results show that the thermal conductivity changes over from a T^n $(n>2)$ dependence for $T>1$ K to a $T^{1.14\pm0.02}$ law at lower temperatures; this is thought to be due to the onset of significant carrier conduction, but the actual temperature dependence of the thermal conductivity below 1 K cannot be accounted for without invoking a lattice component which decreases much more slowly than the variation expected if boundary scattering dominates. The thermopower S is negative and below 2 K behaves linearly with temperature. The magnitude and slope of the thermopower increases with increasing structural imperfection of the samples. For $T>2$ K, the thermopower flattens as it approaches the onset of the phonon drag anomaly observed earlier near 7 K.[25] In view of the anomalous behavior of the lattice thermal conductivity and the general importance of the HOPG material, it seems essential that precise specific-heat measurements at temperatures well below that of liquid helium be carried out.

ACKNOWLEDGMENTS

Samples of HOPG were kindly provided by Dr. A. W. Moore of Union Carbide. We wish to thank Professor W. P. Pratt and Professor P. A. Schroeder for thermometer calibration and Mr. J. Cohn and Mr. R. Hockey for help with measurements. We are grateful to Professor A. K. McCurdy for sending us his unpublished calculations on the thermal conductivity of graphite and to Professor R. Clarke for fruitful discussions and critical reading of the manuscript. The work was supported by the National Science Foundation Low Temperature Physics Program Grant No. DMR-83-04356.

---

[1] D. T. Morelli and C. Uher, Phys. Rev. B **30**, 1080 (1984).

[2] Germanium thermometers are manufactured by Lake Shore Cryotronics and have been calibrated at the Michigan State University against sensors which are traceable to the National Bureau of Standards.

[3] W. P. Pratt, Jr., C. Uher, P. A. Schroeder, and J. Bass, in *Proceedings of the International Conference on Thermoelectricity in Metallic Conductors, East Lansing, Michigan, 1977,* edited by Frank J. Blaff and Peter A. Schroeder (Plenum, New York, 1978).

[4] R. Berman, Proc. Phys. Soc. London Sect. A **65** 1029 (1952).

[5] G. A. Slack, Phys. Rev. **127**, 694 (1962).

[6] C. A. Klein and M. G. Holland, Phys. Rev. **136**, A575 (1964).

[7] M. G. Holland, C. A. Klein, and W. D. Straub, J. Phys. Chem. Solids **27**, 903 (1965).

[8] B. T. Kelly, Carbon **6**, 71 (1968).

[9] W. DeSorbo and G. E. Nichols, J. Phys. Chem. Solids, **6**, 352 (1958).

[10] K. Komatsu, J. Phys. Chem. Solids, **6**, 380 (1958).

[11] B. J. C. van der Hoeven, Jr., and P. H. Keesom, Phys. Rev. **130**, 1318 (1963).

[12] Essentially identical behavior of the in-plane thermal conduc-

tivity of graphites (both Union Carbide and la Sociète "Le Carbone-Lorraine" materials) is presented in the Ph.D. thesis of Dr. Claude Ayache. We thank Dr. Ayache for bringing this to our attention.

[13] We rule out scattering by vibrating, or "fluttering," dislocations since these in general produce an anomalously *fast* temperature dependence.

[14] K. Komatsu and T. Nagamiya, J. Phys. Soc. Jpn. **6**, 438 (1951).

[15] J. M. Worlock, Phys. Rev. **147**, 636 (1966).

[16] D. Walton, Phys. Rev. **157**, 720 (1967).

[17] J. Krumhansl and H. Brooks, J. Chem. Phys. **21**, 1663 (1952).

[18] I. L. Spain, Chem. Phys. Carbon **16**, 119 (1980).

[19] S. Amelinckx, P. Delavignette, and M. Meerschap, Chem. Phys. Carbon **1**, 1 (1965).

[20] A. K. McCurdy, H. J. Maris, and C. Elbaum, Phys. Rev. B **2**, 4077 (1970).

[21] A. K. McCurdy, in *Proceedings of the 18th International Conference on Thermal Conductivity, Rapid City, SD (1983)*, edited by T. Ashworth (Plenum, New York, in press).

[22] W. D. Gauster and I. J. Fritz, J. Appl. Phys. **45**, 3309 (1974).

[23] R. Berman, *Thermal Conduction in Solids* (Clarendon, Oxford, 1976).

[24] C. Ayache and I. L. Spain, Philos. Mag. B **42**, 597 (1980).

[25] C. Ayache, A. de Combarieu, and J. P. Jay-Gerin, Phys. Rev. B **21**, 2462 (1980).